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GLASS ENAMELS FOR STEEL AND CAST-IRON ARTICLES (Review)

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Various types of enamels for steel and cast iron are analyzed. Their chemical compositions and main physicochemical properties are considered. The current state of research in the synthesis of new enamels and improvement of the physicomechanical properties of existing glass enamels is discussed. The possibilities of replacing costly material components in enamels by less expensive and more available materials as well as recycled waste are specified.

Ferrous metals are liable to corrosion, due to which their losses amount to about 10% of the world output. Different coatings are used to protect metals from corrosion. Enamel deposited on a metal article and fixed in firing produces a vitreous coat which protects the article from the effect of different liquid, gaseous, and solid reactants.

Coatings are divided into two types: single-layer and double-layer. The single-layer coating is more advantageous from the point of view of energy, and yet so far double-layer coatings prevail in the industry.

Two types of enameling are used for double-layer enameling: undercoat enamel and surface enamel. Double-layer coating is usually applied due to the difference in the TCLE of the surface enamel and the metal substrate. The undercoat enamel is an intermediate layer between the metal and the surface enamel. The TCLE of undercoat glass should be 10 – 25% below the metal TCLE, and the TCLE of surface enamel should be 15% higher than the undercoat TCLE [1].

Although the variety of undercoat enamels is extensive, they all consist of a limited set of components (mostly SiO_2, B_2O_3, Al_2O_3, Na_2O or K_2O, CaO, fluorides, and adhesive oxides).

The most widely applied adhesive oxides are cobalt and nickel oxides, which are costly and scarce in supply, although they are introduced in relatively small quantities: from 0.1 to 3.0% (here and elsewhere, weight content is indicated). A decrease in the content of these oxides in undercoat enamels makes it possible to decrease the production cost of enameled products. Some data [2] indicate that ferric and manganese oxides can also facilitate adhesion, like cobalt and nickel oxides. The conversion of Mn^{3+} into Mn^{2+} is fully completed only in the course of burning in and contributes to the adhesion of undercoat enamel to steel. Currently, there is a trend toward developing enamels poor in cobalt or totally free of cobalt. The problem of developing undercoat enamel frits for steel without traditional effective adhesion activators has been repeatedly discussed in our country [3] and abroad and remains debatable. Polish researchers [4] studied the possibility of replacing CoO in the composition of undercoat enamels with CuO. The optimum content of CuO ranges from 3.8 to 4.8%. In their strength of adhesion to steel and other properties they are not inferior to the cobalt-containing undercoat enamels.

Mixtures for sheet-steel undercoat enamels mostly contain expensive and scarce raw materials. In order to decrease the production cost of enamels and save resources, the Ural Research Institute of Ferrous Metals [5], the Institute of General and Inorganic Chemistry of the Belarus Academy of Sciences, the Institute for Construction of Main-Lines (USSR Inventor's Certif. 58131), and Novocherkassk State Technical University [6] carried out research intended to replace costly raw materials by industrial waste, such as metallurgical slags.

The requirements on undercoat enamels for cast iron virtually coincide with the requirements imposed on undercoat coatings for steel. Undercoat enamels for cast iron can be sintered and fritted (for wet surface enameling) or melted undercoats (for powder enameling).

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Fritted undercoat enamels for cast iron significantly differ from undercoat enamels for steel. Undercoat coatings for steel should necessarily include oxides facilitating the coat adhesion to steel. Adhesion of an undercoat layer to cast iron is mechanical due to the penetration of the undercoat into the pores of the rough and strongly irregular cast-iron surface. Therefore, undercoat layers for iron contain small quantities of adhesion oxides (around 0.5%) or none at all. Another specific feature of undercoats for iron is the need for introducing a great amount of high-melting components incapable of totally melting in firing. Fritted (sintered) undercoat enamels in sintering should not transform into a continuous vitreous layer but only sinter to a highly porous state. Such a layer is more elastic than a vitreous layer. The high porosity is necessary, since cast iron contains a great number of impurities which oxidize under firing and form gases, whose volume cannot transgress via the undercoat without damaging consequences.

Melted undercoat enamels for iron are similar to undercoat enamels for steel but are harded and, like fritted undercoat coats, contain few adhesive oxides or none at all. They contain less alkaline metal oxides than undercoat enamel for steel. They are deposited on iron in such a thin layer that the undercoat layer after firing is virtually invisible. This distinguishes them from fritted undercoats.

All undercoats for cast iron necessarily contain a great amount of boric anhydride; coats without boron are not used, since an increased content of boric oxide is necessary for good wetting and adhesion.

Undercoats for steel and iron used in the enameling industry are not as varied in their composition as surface enamels (Table 1).

Surface enamels are usually based on opacified glasses which impart a softer tone to enamels. The main opacifiers are zirconium compounds, tin oxide, titanium dioxide, arsenic compounds, and phosphates, whereas such compounds as sodium fluoride, fluorspar, cryolite, and sodium silicofluoride belong to auxiliary opacifiers which make the enamels opaque only in the presence of the main opacifiers.

Depending on the type of opacifier used, surface enamels for steel are subdivided into fluorine, antimonic, zirconium, titanium, tin, etc. Fluorine coats contain from 6 to 12% fluorine. In melting frit of this enamel, fluorine is released, which pollutes the ambient medium; therefore, special enamel compositions not containing fluorine were developed [7]. Opacification using fluorine compounds without introducing additional opacifiers is very weak. Antimonic enamels are mostly used in the production of refrigerators, kitchen stoves, and signs. Their use for kitchen utensils is prohibited due to the formation of poisonous trivalent antimony. Zirconium enamels, despite some virtues (safety, stability at any temperature, good opacification), did not become widespread, since the introduction of zirconium oxide sharply increases their viscosity. The most commonly used at present are surface titanium enamels, since they have high opacification allowing for a thin one-layer coating and have good chemical, mechanical, and thermal parameters and high luster. At the same time, they are significantly cheaper than other white enamels.

It is possible to add various colorants and pigments to white-enamel mixtures in milling and thus obtain surface enamels of various colors and shades.

Surface enamels for cast iron are distinguished by their deposition method: wet (slip) and dry (powder). Enamels deposited after wet milling virtually do not differ in their composition from standard surface enamels for steel. Under certain conditions, enamels for steel can be deposited in the form of melt on cast iron as well. Powder enamels have to be relatively low-melting in order to adhere to a hot substrate and yet not spread over it. These enamels should contain less SiO_2 and Al_2O_3 and more B_2O_3, ZnO, BaO, and fluoride than the surface enamels for steel. Some surface enamels for cast iron were developed based on titanium enamels with a high degree of whiteness [8].

Along with the standard method of metal enameling, one-coat (without an undercoat) type of enameling is currently being developed [10 – 14]. Enameling without an undercoat layer is of great practical significance, since this makes it possible to reduce the consumption of raw materials and shorten the enamel processes and does not require costly adhesive oxides. The most widespread are white titanium enamels used as single-layer coats for household articles. In order to achieve a high quality for a single-layer coating and strong adhesion to the metal, the metal should be prepared for enameling by special methods. Because of the complexity of these methods, single-layer enamels are not yet widely used. There are some studies in the field of synthesis of one-coat enamels for steel, and certain papers [15] discuss the development of one-coat enamels for iron.

The studies in [16, 17] investigated the possibility of one-fire, two-coat enameling. The undercoat in this case consists of adhesive suspensions based on finely pulverized frits rich in adhesive oxides and containing alkaline-earth metal oxides as well. This method requires thin and compact deposition of the undercoat and surface enamel coat on metal, which is hard to accomplish owing to the emerging defects. The use of mono- and dialuminum phosphates as binding additives and composite CuO : MoO and $Al(OH)_3 + H_3PO_4$ as functional components made it possible to obtain experimental enamels with the specified properties. However, since certain technological and scientific problems have not been solved, this method has not found wide application.

The main properties of undercoat, surface, and one-coat enamels and enamel coatings are different (Table 2).

The most significant properties required of undercoat enamels are high wettability of the oxidized metal surface by the undercoat melt in firing and strength of adhesion of the undercoat to the metal, spreadability ensuring a continuous undercoat layer, and a wide firing interval allowing for the use of an undercoat in combination with various enamels. The firing interval and fusibility are of great importance for undercoat enamels. The oxidation of steel, type of gas emis-

sion, and completeness of adhesion-forming reactions depend on the firing interval of the undercoat enamel.

In contrast to undercoat enamels, surface enamels have to meet a series of other supplementary requirements determined by the destination of the enameled article. Along with reliable resistance to the action of water, food acids, and alkaline detergents, the enamel coating of articles subjected to heating should have high thermal resistance, overlap the undercoat reliably, and have good exterior outlook, color, and luster, and high mechanical strength [18].

A single-layer coating should combine the properties of undercoat and surface enamels.

The methods used to evaluate the properties of enamels and enameled articles are most fully described in [19].

TABLE 1

Composite	Weight content, %														Destination	Reference
	SiO_2	MnO_2	TiO_2	Al_2O_3	B_2O_3	Fe_2O_3	Na_2O	K_2O	Li_2O	CaO	BaO	MgO	CuO	other		
							Undercoat enamels									
1	27.43	2.38	–	7.75	15.00	0.27	21.57	0.28	–	14.75	–	5.16	–	3.0 Ni_2O_3, 2.4 F	For steel	USSR Inv. Certif. 141714
2	29.10	5.10	–	5.90	17.00	0.40	9.20	–	–	3.20	24.60	0.70	–	1.1 NiO, 0.8 CoO	The same	USSR Inv. Certif. 485856
3	43.20	3.90	1.10	5.80	12.60	1.40	18.40	–	–	3.90	–	0.90	–	1.0 Co_2O_3, 3.9 CaF_2	The same	USSR Inv. Certif. 461073
4	69.00	–	1.50	0.60	1.50	–	8.00	1.70	7.10	2.00	–	–	–	3.0 SnO_2, 2.7 ZnO, 1.1 P_2O_5	The same	USSR Inv. Certif. 460259
5	33.90	8.70	–	7.00	17.50	0.70	9.50			5.30	13.40	1.10	–	0.8 CoO, 1.2 NiO	The same	USSR Inv. Certif. 442160
6	50.90	0.40	0.30	0.70	–	–	23.30	–	4.90	10.80	–	0.50	0.70	1.4 NiO, 0.6 P_2O_5	The same	USSR Inv. Certif. 710997
7	66.20	–	–	1.04	–	0.10	9.29	6.47	4.69	–	–	–	–	9.6 SrO, 1.0 Cr_2O_3	The same	USSR Inv. Certif. 590275
8	49.70	3.40	1.30	0.70	–	–	21.70	–	5.40	9.80	–	–	–	1.0 SrO, 0.4 CoO, 6.6 F	The same	USSR Inv. Certif. 551279
9	32.00	6.80	4.50	5.00	18.00	5.20	2.20	0.20	–	3.20	–	–	–	1.0 CoO, 0.3 NiO	The same	USSR Inv. Certif. 709580
10	40.00	3.00	3.50	2.60	16.00	0.30	22.00	2.00	–	5.30	–	–	–	0.9 CoO, 0.4 NiO, 4.0 F	The same	USSR Inv. Certif. 544741
11	42.70	–	–	6.40	13.40	1.10	28.60			4.80	–	0.30	–	0.3 CoO, 2.0 Ni_2O_3	The same	USSR Inv. Certif. 632662
12	67.53	–	–	6.06	11.00	0.60	10.43	–	–	–	–	–	–	1.7 CaF_2	Fritted, cast iron	[1]
13	57.00 – 68.00	0.50	–	4.00 – 6.00	12.00 – 19.00	0.30	12.00 – 15.00			2.00 – 3.00	–	–	–	–	Melted, cast iron	[2]
							Surface enamels									
14	29.00	–	9.00	17.00	15.30	–	14.00	–	–	13.60	–	–	–	–	For steel	USSR Inv. Certif. 1165653
15	38.56	–	17.30	4.46	19.80	–	15.93	–	–	–	–	1.50	–	2.0 P_2O_5	The same	[2]
16	53.00	–	18.00	13.00	5.00	–	1.00	3.00	–	7.00	–	–	–	–	For iron	[8]
17	47.00	–	1.00 – 4.00	4.00 – 6.00	10.00 – 20.00	–	13.00			2.00	–	–	–	7.0 Na_3AlF_6	Slip, for iron	[2]
18	31.40	–	–	6.70	16.00	–	19.50	–	–	2.60	8.20	–	–	6.8 ZnO, 9.0 Sb_2O_5, 4.9 F	Powder, for iron	[9]
19	41.90	–	–	2.50	4.80	–	19.60	–	–	3.40	4.80	–	–	13.0 ZnO, 6.0 Sb_2O_5, 7.0 F, 3.8 PbO	The same	[9]
							One-coat enamels									
20	32.00	–	5.00	3.00	20.00	–	20.00	2.30	–	6.00	–	–	–	5.0 ZrO_2, 1.0 Co_2O_3, 4.1 F	For steel	USSR Inv. Certif. 687012
21	55.00	1.80	4.60	1.00	3.00	1.00	18.00	1.00	–	3.70	1.40	–	0.40	3.0 CaF_2, 1.0 NiO	The same	USSR Inv. Certif. 1430377
22	65.00	–	2.00	–	8.10	–	13.20	3.30	–	2.40	–	–	–	1.0 P_2O_5, 1.0 V_2O_5	The same	USSR Inv. Certif. 1694498
23	25.00 – 30.00	–	16.00 – 18.00	2.00 – 3.00	11.00 – 16.00	–	17.00 – 22.00	8.00 – 12.00	7.00 – 9.00	–	–	–	–	2.0 P_2O_5	The same	[10]
24	58.50	–	2.00	1.50	8.00	–	18.00		3.00	6.00	–	–	–	1.5 PbO, 1.5 CoO	Acid-resistant	[2]

A new line of synthesis of enamel coats using the sol-gel technology has been recently developed [20 – 22]. This frit-free method makes it possible to exclude such power-consuming stages as enamel melting from the enamel production process. The frit-free technology consists of preparing a solution containing compounds which disintegrate into oxides, forming a coating under heat treatment at lower temperatures than in firing traditional enamels. Such a solution acts as a vitreous matrix to which ceramics and other fillers are added.

Certain enamels have been synthesized which are capable of long-term service at high temperatures (above 500°C) and are known as heat-resistant enamels. They have to withstand high temperatures and should not react with the metal substrate and ambient medium under a long-term effect of high temperatures. All heat-resistant enamels need to have a high softening point. Devitrified glass (Sital) and glass ceramic coatings are the most promising as heat-resistant coats [23 – 26]. They have a higher softening point than the usual enamels.

Currently, extensive research in the synthesis of new kinds of enamels and improvement of the properties of existing enamels is being carried out in Russia and abroad. The development of compositions and technological parameters

TABLE 2

Composite*	Melting temperature, °C	Melting duration, min	Firing interval, °C	Temperature, °C		Firing duration, min	Adhesion strength, %	Impact strength, kgf · m	TCLE, 10^{-7} °C^{-1} in temperature interval 20 – 400°C	Spreadability, m (at temperature, °C)	Luster, %	Whiteness, %	Heat resistance, °C	Reference
				softening	firing									
							Undercoat enamels							
1	1300	Unknown	790 – 860	490	820 – 840	2 – 3	96	Unknown	98.4	3.92 (850) 5.49 (875)	Unknown	–	Unknown	USSR Inv. Certif. 141714
2	1150 – 1200	90	680 – 740	480 – 565	Unknown	3 – 8	90 – 98	0.8 – 1.0	97 – 109	No data	68 – 80	–	350 – 450	USSR Inv. Certif. 487856
3	1190 – 1200	80 – 90	780 – 840	515	The same	3 – 6	90 – 98	Unknown	108	41.0 (850)	Unknown	–	Unknown	USSR Inv. Certif. 461073
4	1250 – 1300	180 – 240	860 – 920	Unknown	900	60 – 180	90 – 98	1.1 – 1.3	Unknown	No data	The same	–	460 – 480	USSR Inv. Certif. 460259
5	1100 – 1150	60 – 120	730 – 820	The same	Unknown	3 – 8	90 – 98	0.02 – 0.01	83.3 – 100.0	The same	40 – 60	–	300 – 500	USSR Inv. Certif. 442160
6	1280 – 1300	100 – 120	720 – 800	398	The same	3 – 6	90 – 98	Unknown	165.7	The same	Unknown	–	Unknown	USSR Inv. Certif. 710997
7	1300 – 1330	180	840 – 960	Unknown	860 – 880	2 – 3	90 – 98	The same	–	29.54	The same	–	230 – 250	USSR Inv. Certif. 590275
8	1280 – 1300	100 – 115	700 – 800	The same	Unknown	3 – 6	90 – 98	The same	–	42.0 (750) 62.0 (800)	The same	–	Unknown	USSR Inv. Certif. 551279
9	1150 – 1160	65	700 – 970	The same	700	3.5	90 – 98	0.12	–	No data	The same	–	The same	USSR Inv. Certif. 709580
10	1200	95	870 – 900	The same	810	4.5	90 – 98	0.12	–	The same	The same	–	The same	USSR Inv. Certif. 644741
11	1250 – 1300	Unknown	790 – 900	500	850	2 – 3	97.5	Unknown	123	3.72 (850) 4.32 (875)	The same	–	The same	USSR Inv. Certif. 632662
12	1300	The same	850 – 900	Unknown					–	No data	The same	–	The same	[1]
13	1300	The same	850 – 900	The same					–	The same	The same	–	The same	[2]
							Surface enamels							
14	1200 – 1250	90	730 – 810	The same	760	2 – 3	Unknown		–	2.6 (700) 4.9 (750) 6.7 (800) 18.3 (850)	63	89	The same	USSR Inv. Certif. 1165653
15	1300	Unknown	Unknown	720 – 750	820 – 840	1.5 – 3	The same		300	No data	78 – 80	86	The same	[2]
16	1400	The same	The same	Unknown	900	10 – 15	The same		82.6	55.0 (900)	Unknown	85	230 – 240	[8]
18	1200 – 1300	The same	900 – 950	The same	Unknown	Unknown	The same		123	75.0	The same	Unknown		[9]
19	1200 – 1300	The same	900 – 950	The same	The same	The same	The same		114.7	48.0	The same	The same		[9]
							One-coat enamels							
20	1200 – 1300	The same	720 – 820	The same	720	Unknown		0.13	Unknown	No data	The same	Unknown	420	USSR Inv. Certif. 687012
21	1200 – 1300	The same	750 – 900	The same	Unknown	The same		0.60	107	66.0	The same	The same	420	USSR Inv. Certif. 1430377
22	1200 – 1300	The same	750 – 900	The same	The same	The same		0.60	253.6	No data	The same	The same	420	USSR Inv. Certif. 1684498
23	1150 – 1180	30	680 – 700	400	The same	5 – 7	80 – 90	Unknown		The same	53 – 60	83 – 88	Unknown	[10]

* There are no data for composites 17 and 24 [2].

of enamels and their synthesis is being carried out at numerous research centers in Russia, as well as Poland (patent 131174, 124331), Japan (pat. 60-112645, 60-42251, 60-118650) and other countries [27].

The main institutions developing compositions and properties for enamels in Russia are the Ural Research Center of Ferrous Metals (increasing adhesion strength and decreasing toxicity of enamels; USSR Inventor's Certif. 451649, 592772, 592772, and 776997), the All-Union Design Institute for Household Electric Equipment (decreasing the temperature and duration of enamel melting, as well as increasing the spreadability and luster of enamels; USSR Inventor's Certif. 709580, 887496, 697419, 644741, 988404, 706345, 1114637, and 1014807), Novocherkassk State Technical University, Volgograd State Technical University (USSR Inventor's Certif. 897723), St. Petersburg Technological University (USSR Inventor's Certif. 1217807), Research Institute of Sanitary Ware (USSR Inventor's Certif. 1183472), and others.

The main organizations studying enameling in the CIS are the Institute of General and Inorganic Chemistry of the Belarus Academy of Sciences (BSSR Inventor's Certif. 477949, 419486, 632662, 6311479, and 920017), Émal'khimmash Research Institute (USSR Inventor's Certif. 495287, 460259, 377302, and 590275), the Brest Construction Engineering Institute (USSR Inventor's Certif. 1248977), Dnepropetrovsk Chemical Engineering University, Riga Technical University, Georgian Technical University, the Institute of Geophysics and Geology of Moldova, the Donetsk Research Center for Gas Equipment "Gazoapparat, "etc.

Analysis of the developed compositions of glass enamels for steel and cast iron showed that they mostly contain expensive material components. The scope of research intended to replace these expensive components is limited; therefore, further research in this field is a priority. It is also expedient to investigate and widely use one-fire and one-coats enamels, which makes it possible to save energy and material resources.

The traditional two-coat enameling technology implies separate firing of the undercoat enamel and the surface enamel, since their melting points are different. A one-fire, double-layer coating excludes the stage of undercoat firing, which shortens the process of producing enameled articles.

Wide application of one-coat enamels makes it possible to develop a technology which eliminates not only firing of the undercoat but the stages of undercoat coat melting and deposition as well.

Undercoat firing temperatures are rather high and reach 970°C. Since the firing temperature of an enamel applied directly on metal is higher than the firing temperature of the same enamel deposited on an undercoat, it is necessary to continue research in the development of low-melting undercoats and one-coat enamels. Such studies were carried out at Dnepropetrovsk Chemical Engineering University [28, 29].

Another topical line of research is decreasing the firing temperatures of glass ceramic coatings. They have high firing temperatures (for devitrified glasses 1050 – 1150°C, for glass ceramics up to 1250°C), which restricts the technological possibilities of their wide application.

Thus, further studies directed toward improving the known compositions and developing new types of enamels will create new technologies oriented toward saving energy and material resources.

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